キャピラリー電気泳動/質量分析法による覚せい剤類の一斉分析法の開発と法科学への応用

Developments of Simultaneous Analyses of Methamphetamine and Related Compounds by Capillary Electrophoresis/Mass Spectrometry (CE/MS) and Applications to Forensic Science

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1. Introduction

In Japan, a stimulant, methamphetamine (MA) accounts for more than half the abused drugs. In analysis of urine sample for proof of MA use, besides a detection of MA, metabolites of MA, amphetamine (AP) and *p*-hydroxymethamphetamine (*p*OHMA) also need to be detected to prove that MA has passed through a body. Furthermore, analysis of MA in urine must be rapid because suspects are often held until the analysis is completed and in order to respect their personal rights.

MA has two enantiomers, and almost all the abused MA is the *d*-isomer in Japan. Recently, mixtures of *d*-MA and *l*-MA also have been abused. In the analysis MA in urine, the chiral analysis is useful for tracing complex routes of illicit manufacture and sale of abused MA. Furthermore, the simultaneous analysis of specific metabolites of compounds that are metabolized to MA, AP, *p*OHMA such as selegiline and dimethylamphetamine (DMA) is essential to distinguish between users of MA and these compounds. The author developed chiral CE/MS methods for MA, its metabolites and specific metabolites of DMA and selegiline in order to prove MA use.

2. Summary

The author has developed an achiral CE/MS method,[1] and a chiral method for MA and its metabolites in urine samples.[2] In the chiral method,[2] common neutral cyclodextrins (CDs) were used as chiral selectors. This method requires a procedure of extraction from urine. While at this division of environmental sciences and engineering, the author examined a method with direct injection of urine to reduce the analysis time. The method does not require pretreatment of urine, but may cause a peak shift because of rich matrices in urine samples. Thus high chiral separation ability is needed for accurate chirality's identification. The chiral separation ability of the method using neutral CDs was not sufficient for the method with direct injection of urine. By using a modified anionic CD, heptakis-(2,3-diacetyl-6-sulfato)-β-CD (DAS-β-CD), high chiral separations of MA and related compounds were obtained.[3] The author developed a method with direct injection of urine using this CD.[4] [Apparatus, Agilent Technologies CE/MS system; capillary, 50 μm i.d. × 100 cm bare fused-silica, 20°C, +30 kV; sample injection, 50 mbar × 12 sec; electrolyte, 1 M formic acid/1 M ammonium formate (10/0.2) (pH 2.0) containing 1.5 mM DAS-β-CD; Sheath liquid, 10 mM ammonium acetate/methanol (50/50, 4 μL/min)] This rapid method was able to analyze not only MA and related compounds but also specific metabolites of DMA and selegiline {DMA-*N*-oxide and desmethyl selegiline (DM-SG)} (Fig. 1), and was successfully used to distinguish users of MA from users of DMA and selegiline. It is very useful for the routine analysis of urine for proof of MA use.

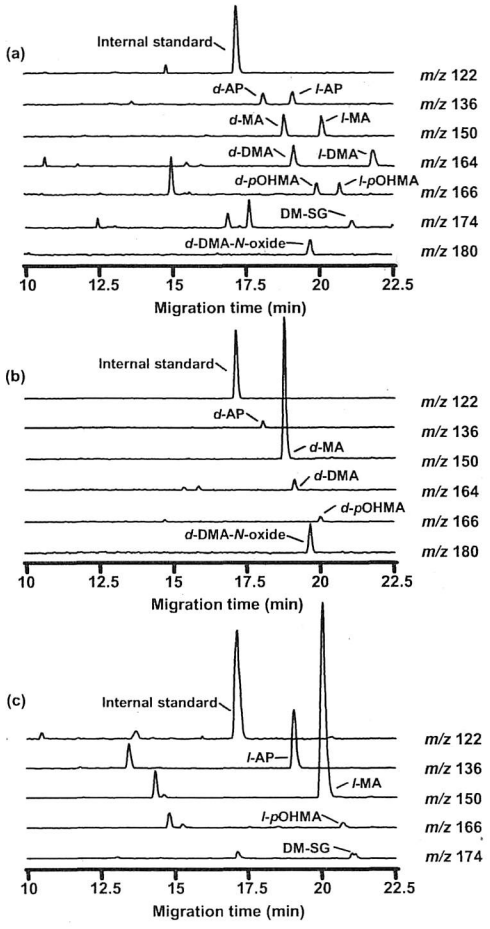

Fig. 1　Mass (Scan) pherograms of (a) a control urine sample spiked with racemic MA and related compounds, (b) a typical urine sample from an addict who used a mixture of *d*-MA and *d*-DMA, (c) a typical urine sample from a patient under selegiline pharmacotherapy.

References

1) Iio, R., Chinaka, S., Tanaka, S. and Takayama, N., *Jpn. J. Sci. Technol. Identification,* 6, 21-26, 2001.
2) Iio, R., Chinaka, S., Tanaka, S., Takayama, N. and Hayakawa, K., *Analyst*, 128, 646-650, 2003.
3) Iio, R., Chinaka, S., Takayama, N. and Hayakawa, K., *Anal. Sci.*, 21, 15-19, 2005.
4) Iio, R., Chinaka, S., Takayama, N. and Hayakawa, K., *J. Health Sci.*, 51, 693-701, 2005.